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# CO<sub>2</sub> Capture From Flue Gas Using Amino Acid Salt Solutions

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The reversible absorption of CO<sub>2</sub> into a chemical solvent is currently the leading CO<sub>2</sub> capture technology. Available solvents are almost exclusively based on aqueous alkanolamine solutions, which entail both economic and environmental complications, making the commercialization of the technology difficult. Amino acid salt solutions have emerged as an alternative to the alkanolamine solutions. A number of advantages make amino acid salt solutions attractive solvents for CO<sub>2</sub> capture from flue gas. In the present study CO<sub>2</sub> absorption in aqueous solutions of 0.5 M potassium glycinate and 0.5 M monoethanolamine (MEA) were performed, using a stirred cell reactor experimental set-up. The absorption of gas containing 10 mol % CO<sub>2</sub> and 90 mol % N<sub>2</sub> was followed by measuring the percentage of CO<sub>2</sub> in the outlet gas. Also the temperature and pH in the solutions were measured during the absorption. The results showed that the CO<sub>2</sub> absorption curves of potassium glycinate and MEA are very similar indicating a potential for potassium glycinate as replacement for MEA in chemical absorption of CO<sub>2</sub> from flue gas. For both the potassium glycinate and the MEA solutions the CO<sub>2</sub> loading capacity was 0.8 mol CO<sub>2</sub>/mol amine and the pH dropped between 2 and 3 units during the absorption process. In both types of solutions the temperature increased as a result of the CO<sub>2</sub> absorption, which is expected due to the exothermic nature of the absorption reaction. The increase in temperature for the potassium glycinate was lower than for MEA indicating a lower heat of absorption/desorption.

# 1 INTRODUCTION

There are a number of technologies available for capturing CO<sub>2</sub> from flue gas, those based on capturing CO<sub>2</sub> after a normal combustion process, are referred to as post-combustion CO<sub>2</sub> capture technologies. The advantage of such technologies is that they don't interfere with the normal combustion process, and they can thus be retrofitted into existing power plants with relative ease. [1 - 2]

## 1.1 Chemical absorption

Chemical absorption is the leading post combustion technique. CO<sub>2</sub> capture by chemical absorption makes use of the temperature dependent reversibility of the chemical reaction between CO<sub>2</sub> and a solvent. Available solvents are almost exclusively based on alkanolamines i.e. molecules that carry both hydroxyl (-OH) and amine (-NH<sub>2</sub>, -NHR, and -NR<sub>2</sub>) functional groups on an alkane backbone. [1,3 - 4] During contact with the flue gas, the alkanolamine solution chemically absorbs the CO<sub>2</sub>; the absorption occurs as a result of reaction with the amine groups. Heating of the CO<sub>2</sub> rich alkanolamine solution leads to release of the CO<sub>2</sub> whereby the alkanolamine solution is regenerated and ready for another round of CO<sub>2</sub> absorption.[1,5] A typical commercial CO<sub>2</sub> capture system using chemical absorption (with alkanolamines as the solvent) is presented in figure 1.

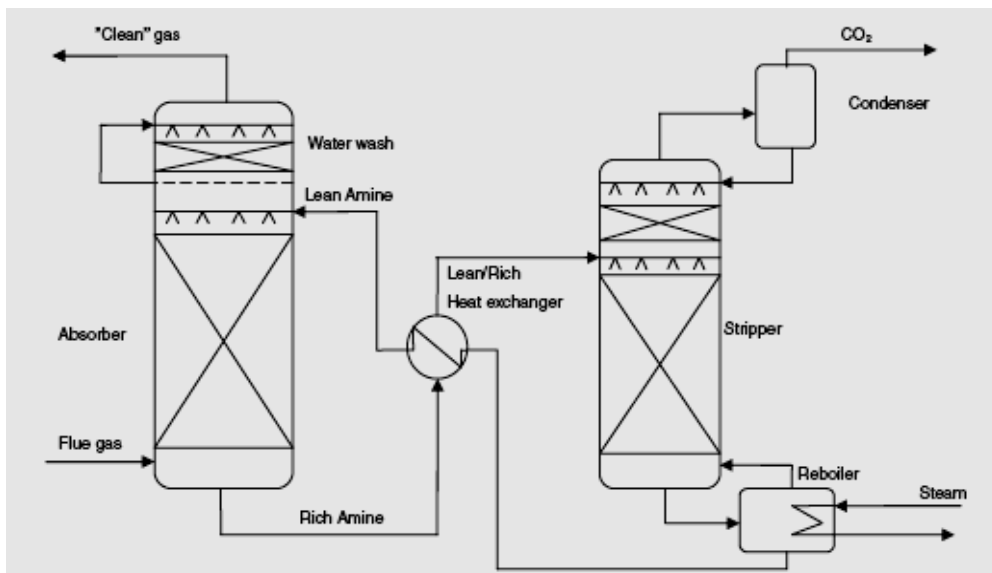


Figure 1: Process flow diagram for CO<sub>2</sub> capture from flue gas by chemical absorption.

### CO<sub>2</sub> absorption

The flue gas is cooled and led into the bottom of the absorber column; the flue gas rises through the column and is hereby contacted by the alkanolamine solution. At absorber temperatures typically between 40 and 60 °C, the alkanolamine solution chemically absorbs the CO<sub>2</sub>. At the top of the absorber column the clean gas with low CO<sub>2</sub> content is released into the atmosphere.

### CO<sub>2</sub> desorption

The rich alkanolamine solution, which contains the chemically bound CO<sub>2</sub> is taken out from the bottom of the absorber column and pumped to the top of the stripper column (also called the desorber). In the stripper the temperature is elevated to about 120 °C, reversing the chemical equilibrium, CO<sub>2</sub> is released and the alkanolamine solution is regenerated. A gas phase consisting only of CO<sub>2</sub> and steam is taken out at the top of the

stripper. The water is separated from the CO<sub>2</sub> in the condenser and the pure CO<sub>2</sub> gas can now be compressed and sent to storage.

### Recycling the solvent

The lean alkanolamine solution at the bottom of the stripper has a low concentration of CO<sub>2</sub> and is pumped back to the top of the absorber column for another round of CO<sub>2</sub> absorption. This way the alkanolamine solution keeps recycling between the absorber and the stripper column transporting the CO<sub>2</sub> between the columns. [1]

CO<sub>2</sub> capture in the described manner is very energy intensive, mostly due to the large amount of heat/energy needed to release the CO<sub>2</sub> from the alkanolamine solution in the stripper. [6 - 7] It has been widely reported that alkanolamines undergo degradation in oxygen-rich atmospheres, such as those typically encountered in the treatment of flue gases, resulting in very toxic degradation products.[6] Besides the economical problem this creates with loss of solvent, there is an increasing environmental concern, due to the possible emission of small amounts of these toxic degradation products to the air.[8] Much research has been and still is centered on examining the various types of alkanolamine solvents with the purpose of optimizing the CO<sub>2</sub> capture process. However the use of alkanolamine solvents for CO<sub>2</sub> capture from flue gas still suffers serious economical and environmental complications and other types of solvents with more favorable characteristics are desirable.

### Amino acid salt solutions for CO<sub>2</sub> capture

Amino acid salt solutions are now being studied as possible alternatives to the alkanolamine solutions. CO<sub>2</sub> absorption using amino acids is a bio-mimetic approach to CO<sub>2</sub> capture, due to its similarity to CO<sub>2</sub> binding by proteins in the blood, such as hemoglobin. Amino acids have the same amine functionality as alkanolamines, and alkaline amino acid salt solutions can be expected to behave similar towards CO<sub>2</sub> in flue gas. But in comparison to alkanolamines amino acid salt solutions have several desirable properties including high stability towards oxidative degradation and low volatility; also they are non-toxic as they are naturally present in the environment. [3, 6] Despite the rising interest few studies have been performed so far on amino acids as absorbents in CO<sub>2</sub> capture systems. The objective of this study was to evaluate the CO<sub>2</sub> capturing ability of the amino acid glycine against that of monoethanolamine (MEA), which is the alkanolamine most widely used for CO<sub>2</sub> capture. The study concentrates on the CO<sub>2</sub> loading capacity (mol CO<sub>2</sub>/mol amine) of solutions of the potassium salt of glycine versus that of MEA.

### The chemical nature of amino acids

Chemically amino acids are molecules having both amine and carboxylic acid functional groups. In biochemistry, the term amino acid most often refers to  $\alpha$ -amino acids with the general structure shown in figure 2 below.[9]

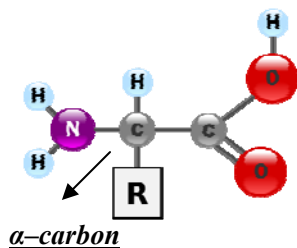


Figure 2: The general structure of a  $\alpha$ -amino acid.

In  $\alpha$ -amino acids, the amine and the carboxylic acid groups are attached to the same carbon, which is called the  $\alpha$ -carbon. The chemical variety of the  $\alpha$ -amino acids comes from the difference in the side chain R, which is an organic substituent also attached to

the  $\alpha$ -carbon. 20 different kinds of amino acids are coded for in the genes of all organisms and incorporated into proteins, these 20 amino acids are called standard or proteinogenic (*meaning protein building*) amino acids. The 20 standard amino acids are all  $\alpha$ -amino acids. Glycine, which is presented in figure 3, is the simplest of all the standard amino acids as it has only a hydrogen atom as its side chain. [10]

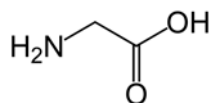
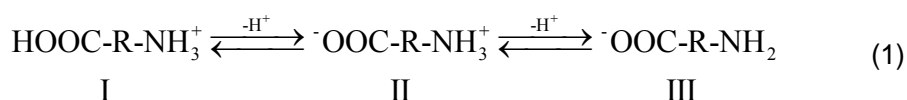


Figure 3: The structure of glycine

### Chemistry of CO<sub>2</sub> absorption into amino acid salt solutions

When a pure amino acid, with the overall formula HOOC-R-NH<sub>2</sub>, is dissolved in water, the following equilibria are established. [11]



The amino acid is predominantly on its zwitterionic form (II), where the carboxylic acid group has lost a proton while the amine group is protonated, and the pH of the solution is equivalent to the isoelectric point of the given amino acid. [11] As CO<sub>2</sub> reacts only with deprotonated amines, the zwitterionic form of the amino acid is incapable of reaction with CO<sub>2</sub>. Hence it is necessary to add an equivalent amount of strong base to deprotonate the amine group and form the negatively charged form of the amino acid (III). The base which is used for this purpose is usually potassium hydroxide, with the potassium salt of the amino acid becoming the active component, which reacts with CO<sub>2</sub>. In the case of glycine the active component becomes the potassium salt of glycine (potassium glycinate), shown in figure 4. [3, 6, 12]

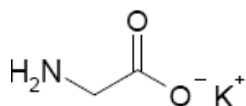
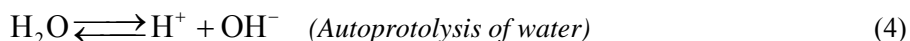
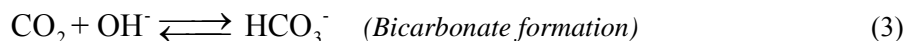


Figure 4: Potassium glycinate

It is generally agreed that alkaline salt solutions of amino acids react with CO<sub>2</sub> similar to alkanolamines having primary or secondary amine functionalities. CO<sub>2</sub> reacts with aqueous solutions of primary or secondary amines, reaching an equilibrium of carbamate and bicarbonate (and if pH is suitable also carbonate). The reactions that occur in the liquid phase are as follows (with the amino acid salt represented as AmA). [4, 6, 11, 13 - 14]



As seen CO<sub>2</sub> absorption can either take place by carbamate formation or bicarbonate formation. There have been conflicting chemical mechanisms proposed to describe the

absorption process. However, it is clear from the reaction rates that the initial absorption reaction is the formation of the carbamate. [3, 5, 11, 13, 14, 15]

## 2 MATERIALS AND METHODS

### 2.1 Chemicals

The 0.5M potassium glycinate solutions were prepared by adding to glycine (>99.9% pure) an equimolar quantity of potassium hydroxide (>85% pure) in a volumetric flask and filling it to the mark with deionized water. The MEA solutions were prepared by adding MEA (>99.5% pure) to a volumetric flask and filling it to the mark with deionized water. All chemicals were purchased from Sigma Aldrich.

### 2.2 Experimental Set-up

The experimental setup used in this study is shown in figure 5a and 5b. It is a stirred cell experimental set-up with a magnetic stirrer (MS). The Analytic cell (AC) is a 1 liter six-necked round-bottom flask. In each CO<sub>2</sub> absorption experiment 0.5L of the prepared 0.5M amine solution (potassium glycinate or MEA) was transferred to the cell. Through one of the inlets a tube connected to a gas cylinder containing synthetic flue gas (SFG) (10 mol% CO<sub>2</sub> and 90 mol% N<sub>2</sub>) was brought into contact with the amine solution. A gas distributor (GD) at the end of the tube insured a high mass transfer area between gas and solution. A flow controller (FC) (Bronkhorst High-Tech) controlled the flow rate of the gas from the gas cylinder to the solution. The gas flow rate in the experiments was 1L gas/min which equals 0.0041mol CO<sub>2</sub>/min or  $6.83 \cdot 10^{-5}$  mol CO<sub>2</sub>/sec.

During the experiment the pH and the temperature of the solution was measured using a pH meter (pH M) (Metrohn 691 pH Meter) and a Pt100 placed in contact with the solution through 2 separate inlets. A CO<sub>2</sub> analyzer (CA) (Vaisala CARBOCAP, Carbon dioxide Transmitter series GMT220) placed in another inlet measured the percentage of CO<sub>2</sub> in the outlet gas throughout the experiment. One inlet was used as a vent, and the last inlet to the cell was closed off. The pH meter, the Pt100, and the CO<sub>2</sub> analyzer were connected to a computer and data from the 3 instruments were collected during the experiment. Each absorption experiment was started by turning on the gas flow and at the same time starting the data collection (DC) program. Data were collected every fifth second resulting in data points of pH, temperature, and percentage CO<sub>2</sub> (in the outlet gas) as a function of time. When the percentage of CO<sub>2</sub> and the pH had been constant (and temperature had been almost constant) for 15 minutes, the system was assumed to be very near equilibrium, and the experiment was terminated.

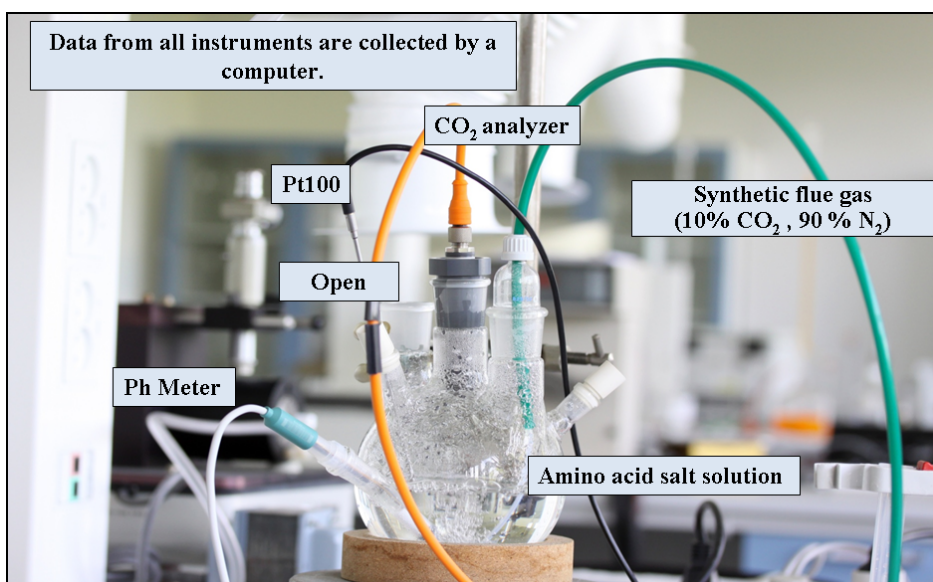


Figure 5a: photo of the stirred cell set-up

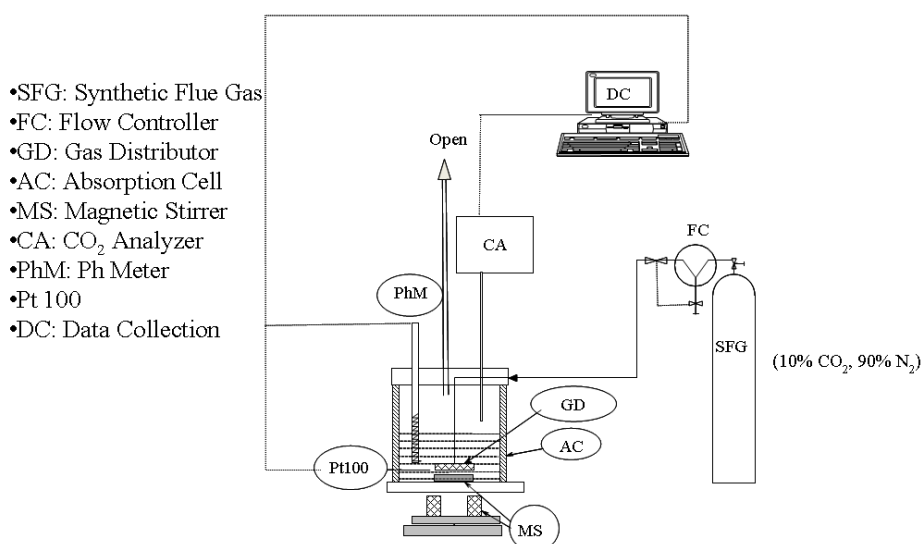


Figure 5b: Schematic representation of the stirred cell set-up

### 3 RESULTS AND DISCUSSION

In this study the CO<sub>2</sub> loading capacity of solutions of 0.5M potassium glycinate were evaluated against that of 0.5M MEA solutions. Figure 6a, 6b and 6c show three curves which are representatives of the obtained results. Figure 6a is a control experiment and shows absorption of synthetic flue gas containing 10 mol % CO<sub>2</sub> and 90 mol % N<sub>2</sub> into 0.5 L deionized water. Figure 6b and 6c show absorption of the same synthetic flue gas into 0.5L 0.5M MEA and potassium glycinate respectively. The curves (6a, 6b and 6c) present the variation of percentage of CO<sub>2</sub> (in the outlet gas) as well as the temperature and the pH of the solutions as a function of time. The curves are shown with a time axis

of 8000 seconds even though the experiments with MEA and potassium glycinate had longer duration.

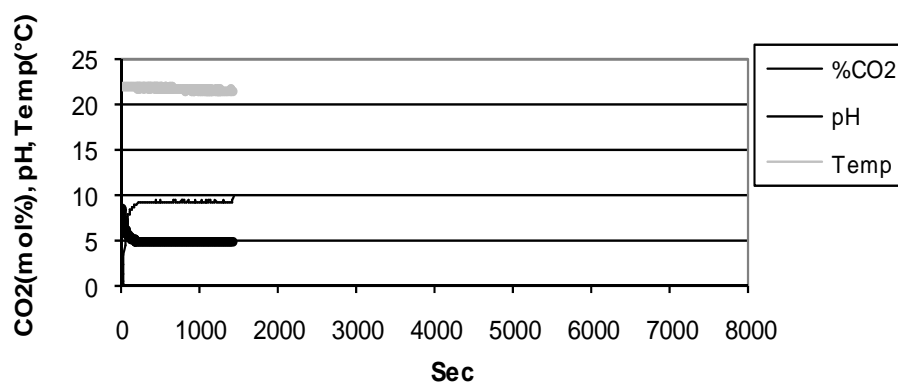


Figure 6a: CO<sub>2</sub> absorption into deionized water

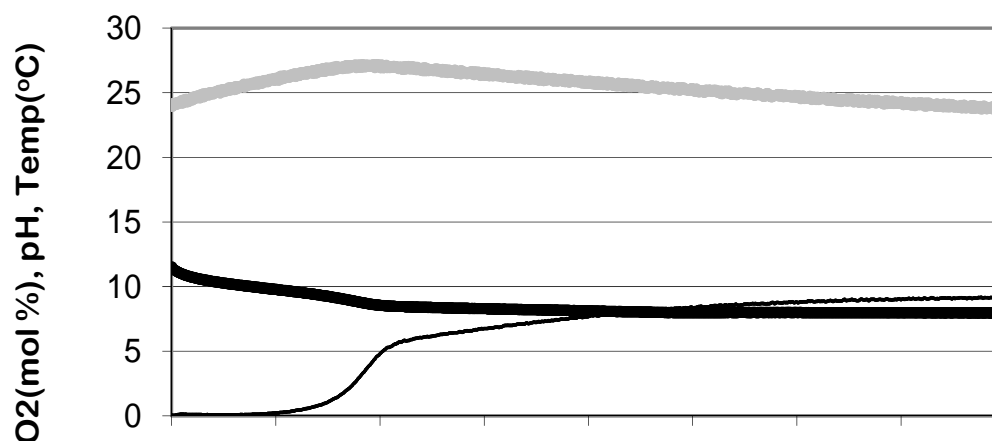


Figure 6b: CO<sub>2</sub> absorption into 0.5L 0.5M MEA.

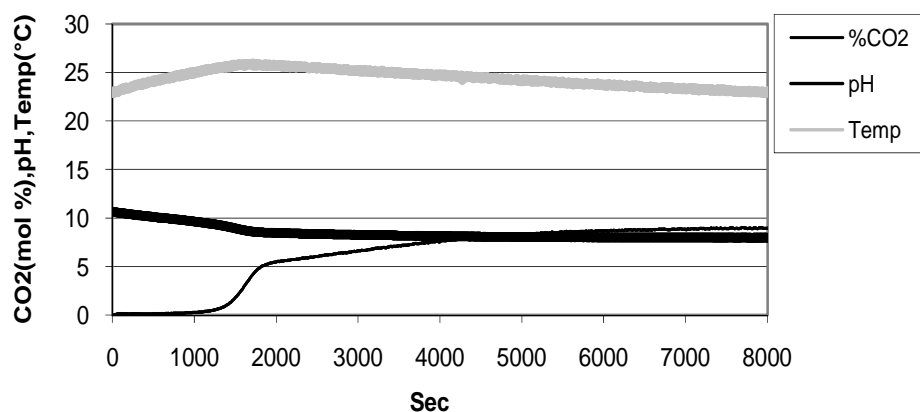


Figure 6c: CO<sub>2</sub> absorption into 0.5L 0.5M Potassium glycinate



## Loading capacity

The CO<sub>2</sub> loading capacity of the solution was obtained by integrating the CO<sub>2</sub> signal (CO<sub>2</sub> in the inlet gas minus the CO<sub>2</sub> in the outlet gas) over time. The CO<sub>2</sub> loading capacity was found to be 0.8 mol CO<sub>2</sub>/mol amine in the case of both the potassium glycinate and MEA solutions indicating that potassium glycinate has the potential for the replacement of MEA in chemical absorption of CO<sub>2</sub> from flue gas. If the reaction was solely due to carbamate formation the maximal loading would be 0.5 mol CO<sub>2</sub>/mol amine as 2 mol amine are used to absorb 1 mol of CO<sub>2</sub> in carbamate formation. The extra loading of 0.3 mol CO<sub>2</sub>/mol amine is due to the fact that bicarbonate formation is also contributing to the absorption. It shall be noted that any physical CO<sub>2</sub> absorption can be ruled out. Physical CO<sub>2</sub> absorption is the absorption of CO<sub>2</sub> in the liquid phase that is not due to chemical reaction. Comparing figure 6a with 6b and 6c it is seen that physical absorption is negligible compared to chemical absorption due to reaction. The loading capacity found for the MEA solution is in very good agreement with what was observed by Mason and Dodge,[16] who did an extensive investigation of the loading capacity of CO<sub>2</sub> in the range of MEA concentrations from 0.5N to 12.5N at temperatures between 0 and 75 °C, partial pressures of CO<sub>2</sub> ranging from 1 to 100 Kpa and total pressure of 1 atm. For the potassium glycinate solution we were not able to find data in literature with which we could directly compare our result, but the good agreement between the literature data and our obtained loading for the MEA solution point to a good reliability of our stirred cell experimental set-up.

## Variation of pH

There is a decrease in pH during the absorption process with CO<sub>2</sub> absorption into both potassium glycinate and MEA solutions. In the case of potassium glycinate the pH declines from 10.6 to 8, and in the case of MEA the pH declines from 11.5 to 9.3. The general decrease in pH coincides with the absorbed amount of CO<sub>2</sub>. This result is expected since CO<sub>2</sub> is an acidic component. This phenomenon is explained by reaction (3) to (4). Apart from carbamate formation in reaction (2), the CO<sub>2</sub> is also being absorbed by bicarbonate formation (3). Bicarbonate formation uses OH<sup>-</sup>, which shifts the autoprotolysis of water (4) to the right producing H<sup>+</sup> causing a decrease in pH. It is seen that the operational pH range for potassium glycinate is lower than for MEA, this is beneficial, since high alkalinity may create steel corrosion problems. The lower pH is preferable having the potential to decrease the CAPEX of the capture plant.

## Variation of temperature

As the temperature is not held constant during the experiment the exothermic nature of the CO<sub>2</sub> absorption results in a temperature increase of the potassium glycinate and MEA solutions. The rise in temperature coincides with the amount of absorbed CO<sub>2</sub>. It shall be noted that the incoming gas is cold and dry. This will affect the temperature. Both the heat capacity of the gas and the evaporation of water may contribute to the cooling of the liquid. Additionally there is a heat loss to the surroundings. These effects are also clearly seen in the control experiment with water, which does not absorb much CO<sub>2</sub>, but the drop in temperature is observed. In the MEA experiment there is a temperature increase of 3.1 °C (from the starting temperature of 24.1 °C to the maximal temperature of 27.2 °C). In the case of potassium glycinate the temperature increase is 2.9 °C (from the starting temperature of 23.0 °C to the maximal temperature of 25.9 °C). The results indicate a decrease in the heat of desorption of 6.45% in the case of potassium glycinate compared to that of MEA.

## 4 CONCLUSION

The objective of this study was to evaluate the CO<sub>2</sub> loading capacity of aqueous solutions containing 0.5M potassium glycinate against that of 0.5M MEA using a stirred cell reactor experimental set-up. The results presented in this paper show that the CO<sub>2</sub>

absorption curves of potassium glycinate and MEA are very similar indicating a potential for potassium glycinate as replacement for MEA in chemical absorption of CO<sub>2</sub> from flue gas. Solutions of 0.5M potassium glycinate and 0.5M MEA both have a CO<sub>2</sub> loading capacity of 0.8 mol CO<sub>2</sub>/mol amine for the given synthetic gas of 10 mol% CO<sub>2</sub>. In addition the results show a lower operational pH area as well as a lower heat of desorption for potassium glycinate compared with MEA, both of which have the potential for a cost reduction of the capture process.

### Acknowledgments

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